PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C11D 7/50	A1	(11) International Publication Number: WO 00/63340
		(43) International Publication Date: 26 October 2000 (26.10.00)

(21) International Application Number: PCT/US00/07865

(22) International Filing Date: 24 March 2000 (24.03.00)

(30) Priority Data:
60/129,736   16 April 1999 (16.04.99)   US

(71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): SHICK, Reed, A. [US/US]; 2470 E. Newcastle Lane, Midland, MI 48640 (US). TUCKER, Christopher, J. [US/US]; 6232 Fairway Pines Court 2, Bay City, MI 48706 (US). CONRAD, Daniel, C. [US/US]; 5767 Echo Ridge, Stevensville, MI 49085 (US). KOVICH, Mark, B. [US/US]; 491 Ansley, St. Joseph, MI 49127 (US). WRIGHT, Tremitchell [US/US]; 51832 Hedge Lane, Granger, IN 46530 (US).

(74) Agent: HILL, Stanley, K.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD AND COMPOSITION FOR REDUCED WATER DAMAGE LAUNDRY CARE

(57) Abstract

A method and composition for laundering a cloth article having reduced water damage in which a solvent having competing adsorption is employed in the method and composition, including a method of determining whether a candidate solvent for use in the method and composition is acceptable.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

METHOD AND COMPOSITION FOR REDUCED WATER DAMAGE
LAUNDRY CARE

This invention relates to the use of certain solvents, particularly organically-based solvents, in a method for laundering clothes or fabrics so that the process provides the feature of reducing the damage done to fibers in the cloth caused by water. Further, a composition is provided to use in the method featured. Finally, there is provided a means for solvent selection according to which a candidate solvent for use in the composition and the laundry method can be selected.

Numerous patents and publications, too many to cite herein, have dealt with the laundry process, but usually from the standpoint of cleaning. The focus of this invention is the reduction of water damage to clothing and fabric which is washed in the normal wash cycle of commercial or home laundry machines. Some fabrics and clothing are shrunk beyond their intended use by water if, inadvertently, they are included in an aqueous laundry process. Such clothing and fabric can only be adequately cleaned by the solvent based dry-cleaning process. However, such a process can be expensive and is not available for home use. It would therefore be quite an advantage to have a home laundry process that could be useful to clean clothing and fabrics subject to water damage, and particularly shrinkage, in a cost-effective, time effective process with reduced water damage. The present invention has the feature that it will reduce water damage, especially shrinkage as well as wrinkling, dye fading, dye transfer, loss of sizing, pilling, felting, fiber weakening and relaxation. While a reduction of any one of these is considered advantageous, reducing the shrinkage and pilling of wool and the shrinkage and spotting on silk and rayon are major advantages.

The features of the invention are provided in a method of laundering a cloth article in an aqueous admixture so that water damage is avoided by contacting the cloth article in the presence of water with a solvent having a competing adsorption with water on the cloth article. Another aspect of this invention provides an aqueous laundry composition for reduced water damage to a laundered cloth article which comprises an adsorbent amount of a least one solvent or blend of solvents which has competing adsorbency with water on the cloth article. In a still further aspect of this invention, there is provided a method of determining suitability of a solvent for use in a reduced water damage laundry composition and method of laundering a cloth article which comprises the steps of

-1-

A)   measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction of said fiber;

B)   determining the Hansen total solubility parameters and radius of interaction of a candidate solvent;

C)   determining the Hansen total solubility parameters and radius of interaction of water;

D)   comparing the Hansen total solubility parameters and radius of interaction of said solvent with that of said fiber so that a sphere generated by the radius of interaction of the solvent intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/solvent relative difference in the two radii;

E)   comparing the Hansen total solubility parameters and radius of interaction of said water with that of said fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii; and

F)   comparing the result of said step D with the result of said step E, such that an acceptable solvent for said reduced water damage laundry composition has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference.

The method for laundering clothing or fabrics according to the present invention protects the fibers in the cloth by preferentially wetting the cloth fibers. However, the wetting takes place on the fiber surface and, thus, prevents the water from contacting and absorbing into the fiber causing water damage. As used in this invention the term water damage refers to shrinkage, wrinkling, dye fading, dye transfer, loss of sizing, pilling, felting, fiber weakening and fiber relaxation. However, many of these types of damage require repeated washing to manifest the damage. In contrast, shrinkage can be seen in only one wash cycle and many of the remaining water damage effects will be manifest in the same cloth after several washings. Therefore, shrinkage water damage is the most important and immediate type of damage. It is also easily measured by standard laboratory tests which correlate well to effects in actual usage.

Without intending to limit the invention to any theory of operation or mechanism of action, it is believed that by preferentially adsorbing on the surface of the cloth fiber a solvent selected for such characteristics, the absorbency of water into the fiber is hindered and, thus, damage caused by water is decreased. This feature is obtained by the method of laundering a cloth article in an aqueous admixture whereby water damage to the cloth

-2-

article is decreased compared to that caused by laundering in water alone, the method comprising contacting the cloth article with a solvent having a competing adsorption on the cloth article and in the presence of water. Adsorption means contact and adhesion of a thin layer of molecules to the surface of a solid body or liquid. Absorption, in contrast, connotes
5   the liquid taking into the bulk of the cloth fiber.

The solvent used in this invention can be selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, a weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamine and aromatic alcohol. Typical of aliphatic alcohols are lower alkyl alcohols such as methanol, ethanol, propanol; unsaturated
10   alcohols, such as, allyl alcohol; cyclic aliphatic alcohols, such as, furfuryl alcohol; and aralkyl alcohols, such as benzyl alcohol. Typical of alkylene glycols are the group consisting of ethylene glycol, propylene glycol, diethylene glycol and triethylene glycol. Non-limiting examples of alkylene glycol ethers are selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol
15   ethyl ether, diethylene glycol methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether. Typical of the weak acids, esters or anhydrides are those selected from the group consisting of formic acid, acetic acid, lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and glycol ether acetate. The typical examples of alkylene amines useful in this invention are selected from the group consisting of
20   ethylenediamine and diethylenetriamine. A preferred alkanolamine is monoethanolamine. Typical of useful aromatic alcohols are those selected from the group consisting of phenol, cresol and resorcinol.

The solvent is contacted with the cloth article in an amount sufficient to reduce or decrease water damage. Because of the different solubility parameters of various fabrics
25   and fibers and the different solvents involved the amount of solvent can be greatly varied. In addition, the temperature of laundering, the amount of agitation and the overall amount of water employed can influence the amount of solvent necessary to reduce or decrease water damage in the method of this invention. In general, it has been found that from about 0.1 to about 15 percent by weight of solvent based on the total weight of the aqueous wash
30   solution or liquid can be used. Preferably, from 1 to about 10 percent by weight of solvent is used, with from about 3 to about 5 percent by weight being most preferred amounts of solvent useful in this invention.

The method of laundering contemplated by the present invention does not rely on any particular type of laundry apparatus and any typical commercial or household washing
35   machine can be usefully employed. Of course, cleaning, while important, is not the

-3-

emphasis of the present invention. Other laundry additives can be employed as are typically useful in laundry operations for cleaning. As is common in such wash applications, the water and solvent are usually combined prior to addition of cloth. Alternatively, the wash liquor, including the solvent can be applied to the cloth in the form of a spray, foam,

5   mist, vapor, immersion, absorbent transfer or by other means. Once applied, mechanical action is used to wash the cloth, fabric, fiber or clothing. After thorough agitation the bulk of the liquid and soil are extracted from the cloth. An additional bulk wash step with the aqueous wash liquor can be carried out and then one or more rinse steps can be employed. The cloth is then dried according to conventional practice, such as by tumble, microwave,

10   convection, reduced pressure, air hang, absorbent or other means of drying.

In a still further aspect of this invention, there is provided an aqueous laundry composition which provides reduced water damage to a laundered cloth article and which comprises an adsorbent amount of at least one solvent or blend of solvents which has competing absorbency with water on the cloth article, clothing, fabric or fiber to be

15   laundered. More particularly, the composition of this invention is described in which the solvent has competing adsorption on the article in relation to water and is non-absorbent on the cloth, clothing, fabric or fiber to be laundered. One of the methods which is useful to determine whether a solvent can be employed in the method and composition of this invention takes advantage of the Hansen total solubility parameters, the radius of

20   interaction and the relative distance of a sphere generated by the radius of interaction calculated in accord with certain equations derived by Hansen. These parameters are used to determine whether a solvent will compete with water to adsorb on the fiber surface, preventing contact with water and, therefore, reducing water damage to the fiber, fabric or cloth. The Hansen solubility parameters are discussed in Chapter 4 of Industrial Solvents

25   Handbook (by Wesley Archer, Marcel Dekker, Inc. publisher), (1996),pages 35-56, which are incorporated by reference as if fully set forth, with respect to the solubility of solvents in resins. Dr. Wesley J. Archer applied the Hansen solubility parameter theory in reformulating solvent-based coatings in an article in American Paint & Coatings Journal, March 2, 1992, pages 38-45, which is incorporated herein by reference as if fully set forth. These articles

30   form the basis for a further aspect of the invention which is a method of determining a suitable solvent for use in a reduced water damage laundry composition which comprises the steps of (A) measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction of the fiber; (B) determining or obtaining the Hansen total solubility parameters and radius of interaction of a candidate

35   solvent; (C) determining or obtaining the Hansen total solubility parameters and radius of

-4-

interaction of water; (D) comparing the Hansen total solubility parameters and radius of interaction of the candidate solvent with that of the fiber so that a sphere generated by the radius of interaction of the fiber intersects with a sphere generated by the radius of interaction of the solvent to obtain a combined fiber solvent relative difference in the two

5   radii of interaction; (E) comparing the Hansen total solubility parameters and radius of interaction of water with those of the fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii of interaction; and (F) comparing the result of step (D) with the result of step (E) such that an acceptable solvent

10   for the reduced water damage laundry composition of this invention has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference. Also, the candidate solvent should have less absorbency than water so as not to cause fiber damage itself from absorption in the fiber.

       Having set forth the general description of the invention, it is now desired to set forth

15   the best mode of carrying out the present invention with respect to the following Examples of the invention in comparison to damage caused by water or by water and a popular standard laundry detergent.

EXAMPLES

20   Cloth fiber damage can be demonstrated as dimensional stability. Dimensional stability can be reported as the percent shrinkage of a cloth after washing treatment. Square cloth pieces, approximately 30 cm on each side were marked with a square pattern approximately 25 cm each side with a Laundry Sharpie marker. The cloth pieces were then washed in a laboratory scale horizontal axis laundry machine. The machine was charged

25   with two liters of wash liquor, followed by the test cloth. The cloth was washed for three minutes at 200 rpm tumble agitation with tumble direction reversals every 30 seconds. The wash liquor was drained and then extracted from the cloth with an 1800 rpm spin cycle for one minute. Two liters of rinse water was added and the cloth again agitated at 200 rpm for one minute. The rinse water was drained and then extracted from the cloth with an 1800

30   rpm spin cycle for one minute. Air-dry the test cloth. Measure the test pattern dimensions, then iron the cloth with a dry iron at the recommended temperature setting, and re-measure the test pattern. Shrinkage was reported as average percent difference from the dimensions of the unwashed and washed test cloth. For comparison wash data for a pure solvent dipropylene glycol n-butyl ether without a water rinse was included.

35

-5-

Acetate

Wash Liquor (weight percent)				% Shrinkage (average)
100%	Water			2.6%
95.4%	Water	4.4%	Tide	2.5%
95%	Water	5%	Methanol	1.7%
95%	Water	5%	diethylene glycol	1.2%
100%	dipropylene glycol n-butyl ether			0.0%

Silk

Wash Liquor (weight percent)				% Shrinkage (average)
100%	Water			4.0%
95.4%	Water	4.4%	Tide	4.4%
95%	Water	5%	n-methyl pyrrolidone	2.1%
100%	dipropylene glycol n-butyl ether			0.1%

Rayon (not ironed)

Wash Liquor (weight percent)				% Shrinkage (average)
100%	Water			10.0%
95.4%	Water	4.4%	Tide	9.8%
95%	Water	5%	diethylenetriamine	4.9%
100%	dipropylene glycol n-butyl ether			0.2%

-6-

Wool

Wash Liquor (weight percent)				% Shrinkage (average)
100%	Water			5.2%
95.4%	Water	4.4%	Tide	5.2%
95%	Water	5%	diethylenetriamine	3.9%
100%	dipropylene glycol n-butyl ether			0.1%

From the above Examples it is clear that shrinkage is reduced when a solvent is used according to the present invention in an aqueous laundry composition. The invention can also be seen to include the method in which the solvent retards the adsorption and absorption of water on the cloth article or fiber by the solvent itself adsorbing on the fiber or cloth article preferentially. A still further aspect of the invention involves the solvent being defined as having competing adsorption on the cloth article in relation to water and the solvent being non-absorbent on the fiber or cloth article. More preferably, the solvent is selected from those having a radius of interaction with the fiber or cloth article which is about 1.5 times or less than the radius of interaction of water with the fiber or cloth article, preferably, the radius of interaction is 1.0 times or less than the radius of interaction of water with the fiber or cloth article.

-7-

CLAIMS:

1.   A method of laundering a cloth article in an aqueous admixture whereby water damage to said article is decreased, said method comprising contacting said article in the presence of water with a solvent having a competing adsorption on said article.

5

2.   The method of Claim 1 wherein said solvent retards the adsorption and absorption of water on said article by adsorbing on said article preferentially.

3.   The method of Claim 1 wherein said solvent has competing adsorption on said article in relation to water and is non-absorbent on said article.

10

4.   The method of Claim 3 wherein said solvent has a radius of interaction with said article which is about 1.5 times or less than the radius of interaction of water with said article.

15

5.   The method of Claim 4 wherein said solvent is selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamine and aromatic alcohol.

20   6.   The method of Claim 5 wherein said solvent is an alipahtic alcohol which is selected from the group consisting of methanol, ethanol, allyl alcohol, propanol, furfuryl alcohol and benzyl alcohol.

7.   The method of Claim 5 wherein said solvent is an alkylene glycol which is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol and triethylene glycol.

25

8.   The method of Claim 5 wherein said solvent is an alkylene glycol ether which is selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.

30

9.   The method of Claim 5 wherein said solvent is a weak acid or ester or anhydride of a weak acid selected from the group consisting of formic acid, acetic acid,

-8-

lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and glycol ether acetate.

10.   The method of Claim 5 wherein said solvent is an alkylene amine which is selected from the group consisting of ethylenediamine and diethylenetriamine.

11.   The method of Claim 5 wherein said solvent is an alkanolamine which is monoethanolamine.

12.   The method of Claim 5 wherein said solvent is an aromatic alcohol which is selected from the group consisting of phenol, cresol and resorcinol.

13.   The method of Claim 3 in which said solvent is present in a water damage reduction amount in the laundry solution for laundering said article.

14.   The method of Claim 13 in which said solvent is present at from about 0.1 to about 15 percent by weight of the total laundry solution.

15.   The method of Claim 14 in which said solvent is present at from about 1 to about 10 percent by weight of the total laundry solution.

16.   The method of Claim 15 in which said solvent is present at from about 3 to about 5 percent by weight of the total laundry solution.

17.   The method of Claim 1 wherein said article is selected from wool, acetate, silk and rayon.

18.   The method of Claim 17 wherein said article is wool and said solvent is propylene glycol phenyl ether.

19.   The method of Claim 17 wherein said article is acetate and said solvent is methanol.

20.   The method of Claim 17 wherein said article is acetate and said solvent is diethylene glycol.

-9-

21.   The method of Claim 17 wherein said article is silk and said solvent is N-methyl pyrrolidone.

5   22.   The method of Claim 17 wherein said article is rayon and said solvent is diethylenetriamine.

23.   An aqueous laundry composition providing reduced water damage to a laundered cloth article, said composition comprising an adsorbent amount of at least one
10   solvent or blend of solvents which has competing adsorbency with water on said article to be laundered than water.

24.   The composition of Claim 23 wherein said solvent has competing adsorption on said article in relation to water and is non-absorbent on said article.

15

25.   The composition of Claim 24 wherein said solvent has a radius of interaction with said article which is about 1.5 to 0.5 times or less than the radius of interaction of water with said article.

20   26.   The composition of Claim 25 wherein said solvent is selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamines and aromatic alcohol.

27.   The composition of Claim 26 wherein said solvent is an alipahtic alcohol
25   which is selected from the group consisting of methanol, ethanol, allyl alcohol, propanol, furfuryl alcohol and benzyl alcohol.

28.   The composition of Claim 26 wherein said solvent is an alkylene glycol which is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol
30   and triethylene glycol.

29.   The composition of Claim 26 wherein said solvent is an alkylene glycol ether which is selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol
35   methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.

-10-

30.   The composition of Claim 26 wherein said solvent is a weak acid or ester or anhydride of a weak acid selected from the group consisting of formic acid, acetic acid, lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and
5   glycol ether acetate.

31.   The composition of Claim 26 wherein said solvent is an alkylene amine which is selected from the group consisting of ethylenediamine and diethylenetriamine.

10   32.   The composition of Claim 26 wherein said solvent is an alkanolamine which is monoethanolamine.

33.   The composition of Claim 26 wherein said solvent is an aromatic alcohol which is selected from the group consisting of phenol, cresol and resorcinol.
15

34.   The composition of Claim 23 in which said solvent is present at from about 0.1 to about 15 percent by weight of the total laundry solution.

35.   The composition of Claim 34 in which said solvent is present at from about 1
20   to about 10 percent by weight of the total laundry solution.

36.   The composition of Claim 35 in which said solvent is present at from about 3 to about 5 percent by weight of the total laundry solution.

25   37.   A method of determining a suitable solvent for use in a reduced water damage laundry composition which comprises the steps of

    A)   measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction
30   of said fiber;

    B)   determining the Hansen total solubility parameters and radius of interaction of a candidate solvent;

    C)   determining the Hansen total solubility parameters and radius of interaction of water;

-11-

D)   comparing the Hansen total solubility parameters and radius of interaction of said solvent with that of said fiber so that a sphere generated by the radius of interaction of the solvent intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/solvent relative difference in the two radii;

E)   comparing the Hansen total solubility parameters and radius of interaction of said water with that of said fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii; and

F)   comparing the result of said step D with the result of said step E, such that an acceptable solvent for said reduced water damage laundry composition has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference.

38.   The method of Claim 37 wherein said candidate solvent further has less absorbency than water.

-12-

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C11D   D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 56975 A (NATURAL CLEAN CO LTD (JP)) 17 December 1998 (1998-12-17)	1-6,9, 12,13, 17, 23-27, 30,33
A	claims 1,9-11,15; example 2	15,16, 34-36

X	EP 0 479 146 A (MIHAMA CORP) 8 April 1992 (1992-04-08)	1-5,8, 17, 23-26,29
A	claims; example 3	13-16, 34-36

X	WO 98 45523 A (RYNEX HOLDINGS LTD) 15 October 1998 (1998-10-15)	1-5,17, 23-26
A	page 8, line 24 - line 26; examples 1,2	13-16, 34-36

	-/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 July 2000	31/07/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Saunders, T

Form PCT/ISA/210 (second sheet) (July 1992)

1

page 1 of 2

Inte   ional Application No

PCT/US 00/07865

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199702 Derwent Publications Ltd., London, GB; Class D24, AN 1997-018022 XP002142989 & JP 08 284062 A (EMYU RAKUSAI KK), 29 October 1996 (1996-10-29)	1-6,17, 23-27
A	abstract	13-16, 34-36
X	US 3 701 627 A (GRUNEWALDER WERNER) 31 October 1972 (1972-10-31)	1-6,8, 17,19, 23-27,29
A	column 2, line 39 - line 48; claim 1; example 1	13-16, 34-36
X	US 5 374 372 A (BROZE GUY ET AL) 20 December 1994 (1994-12-20)	1-5,7,17
A	column 8, line 2 - line 9; claim 1; examples A-G	13-16, 37,38
A	WO 97 25467 A (CYCLO3PSS TEXTILE SYSTEMS INC) 17 July 1997 (1997-07-17) claim 1; example I	1,13-17, 23,34-36
A	DATABASE WPI Section Ch, Week 199628 Derwent Publications Ltd., London, GB; Class F06, AN 1996-272995 XP002142988 & JP 08 113869 A (DAIICHI KOGYO SEIYAKU CO LTD), 7 May 1996 (1996-05-07) abstract	1,17,23

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9856975	A	17-12-1998	JP	11001699 A	06-01-1999
			AU	8236598 A	30-12-1998
EP 0479146	A	08-04-1992	JP	2970933 B	02-11-1999
			JP	4142398 A	15-05-1992
			DE	69123683 D	30-01-1997
			DE	69123683 T	28-05-1997
			ES	2097173 T	01-04-1997
			US	5634947 A	03-06-1997
WO 9845523	A	15-10-1998	US	5888250 A	30-03-1999
			AU	6886698 A	30-10-1998
			EP	0975830 A	02-02-2000
JP 8284062	A	29-10-1996	NONE		
US 3701627	A	31-10-1972	DE	2004232 A	05-08-1971
			CH	553282 A	30-08-1974
			FR	2077423 A	22-10-1971
			GB	1305001 A	31-01-1973
			NL	7018870 A	03-08-1971
US 5374372	A	20-12-1994	AU	7563094 A	21-03-1995
			WO	9506102 A	02-03-1995
WO 9725467	A	17-07-1997	US	5763382 A	09-06-1998
			AU	1536197 A	01-08-1997
			US	5645608 A	08-07-1997
JP 8113869	A	07-05-1996	NONE		

Form PCT/ISA/210 (patent family annex) (July 1992)